Unified treatment of $A + B \rightarrow 0$ and $A + A \rightarrow 0$ chemical reactions through Thompson's approach.

Cláudio Nassif *and P.R.Silva

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Departamento de Física - ICEx - UFMG
Caixa Postal 702 - 30.123-970 - Belo Horizonte - MG - Brazil

Abstract

In this work we propose an action to describe diffusion limited chemical reactions belonging to various classes of universality. This action is treated through Thompson's approach and can encompass both cases where we have segregation as in the $A + B \rightarrow 0$ reaction, as well the simplest one, namely the $A + A \rightarrow 0$ reaction .Our results for long time and long wavelength behaviors of the species concentrations and reaction rates agree with exact results of Peliti for $A + A \rightarrow 0$ reaction and rigorous results of Bramson and Lebowitz for $A + B \rightarrow 0$ reaction, with equal initial concentrations.The different classes of universality are reflected by the obtained upper critical dimensions varying continuously from $d_c = 2$ in the first case to $d_c = 4$ in the last one. Just at the upper critical dimensions we find universal logarithmic corrections to the mean field behavior.

1 Introduction

Since the pioneering work of Ovchinnikov and Zeldovich (O Z)[1], followed by Toussaint and Wilczek [2], the study of the chemical reactions between

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*e-mail: cnassif@fisica.ufmg.br

two diffusing species which annihilate each other or combine to form an inert product when they meet, has becomming a subject of increasing interest [1 to 8]. As has been recognized since O. Z. work[1] (see also [2] and [3]), the spatial fluctuations in the particle density plays a basic role in the long time behavior of their concentrations. Then classical kinetics of reactions rates become the proper description of this matter, only above some upper critical dimension.

Early treatments considered situations starting with equal or unequal homogeneous concentrations of the two reactant species [1 to 8], but more recent studies have also been adressed to the case of inhomogeneous initial conditions [9 to 11].

A simple example of diffusion limited reaction is given by $A+A \rightarrow 0$ (inert product). A field theory description of this reaction was proposed by Peliti [12], performing the renormalization of it at all orders in the perturbation theory.

Krug [13] has proposed a continuous version of a diffusion limited annihilation (DLA) reaction with a point source. Based on the work of Krug [13], one of the present authors [14] wrote na action that when treated by the method of the dimensions due to Thompson [15], reproduced the exact results of Peliti [12] for the $A + A \rightarrow 0$ reaction. Thompson's method [15] could be though as an alternative approach to the renormalization group formalism [16].

Some important results obtained by Peliti [12] is that the long time behavior of the concentration of species A is given by

$$\langle \epsilon \rangle \sim \begin{cases} t^{-\frac{d}{2}}, & d < 2 \\ \frac{\ln(t)}{t}, & d = 2 \\ t^{-1}, & d > 2, \end{cases} \tag{1}$$

where $d_c = 2$ is the upper critical dimension, namely the dimension above which the system behaves classically.

On the other hand Bramson and Lebowitz[5] performed a rigorous treatment looking for the long time behavior of the concentrations $\langle \epsilon_A \rangle$ and $\langle \epsilon_B \rangle$ of two different species in the reaction $A + B \rightarrow 0$, both for equal and unequal initial concentrations of the two species. In the case of equal initial concentrations, namely when $\langle \epsilon_A \rangle_0 = \langle \epsilon_B \rangle_0$, they found that:

$$\langle \epsilon_A \rangle = \langle \epsilon_B \rangle \sim \begin{cases} t^{-\frac{d}{4}}, & d < 4 \\ t^{-1}, & d > 4, \end{cases} \qquad (2)$$

being $d_c = 4$ the upper critical dimension in this kind of two species annihilation reaction.

A heuristic method as a means to obtain scaling laws for $A + A \rightarrow 0$ and $A + B \rightarrow 0$ reactions was developed by Lindenberg, Shen and Kopelman (LSK [17]). LSK work was concerned with the study of the above reactions both in euclidian and in fractal geometries and they found that

$$\langle \epsilon \rangle \sim t^{-\alpha} \qquad (3)$$

where

$$\alpha = \frac{d_s}{2} \left[1 - \frac{\gamma d_s}{2d_f} \right] \qquad (4)$$

In (4), d_f and d_s are respectively fractal and spectral dimensions, and the proper choise of γ leads to the description of a specific kind of reaction. As example, in euclidian geometries, putting $d_s = d_f = d$, we must choose $\gamma = 1$ for the $A + B \rightarrow 0$ reaction and $\gamma = 0$ for the $A + A \rightarrow 0$ reaction.

The aim of this paper is to apply Thompson's method [15] to study the long time behavior of some different kinds of diffusion limited reactions.

C. J. Thompson [15] proposed a simple heuristic method as a means to study the critical behavior of a system undergoing second order phase transition. He started from a Landau-Ginsburg-Wilson free energy or hamiltonian, and was able to get an explicit relation for the correlation length critical exponent (ν) as a function of the lattice dimensionality (d). If we think that this Φ^4- theory is within the same class of universality of the Ising model, Thompson's work reproduces the exact results for $\nu(d = 2) = 1$ and $\nu(d = 1) \longrightarrow \infty$.

Thompson's method has been applied to obtain the correlation length critical exponent of the Random Field Ising Model by Aharony, Imry and Ma [18] and by one of the present authors [19]. His method was also used to evaluate the correlation critical exponent of the N-vector Model [20]. Yang-Lee Edge Singularity Critical Exponents [21] has been also studied by this method. In section 2, we propose an action to describe the $A + B \rightarrow 0$ reaction and we treat it through the Thompson 's approach. This action has

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been evaluated as an extension of that employed in a previous work [14] in order to treat the $A + A \rightarrow 0$ reaction, and in doing this, an important novel ingredient to be considered is segregation. As we will see our treatment is able to reproduce some of Bramson and Lebowitz results [5]. In section 3 we pursue further on this subject, and propose a generalized action which reproduces the achievements of section 2 and those of the previous work [14] as particular cases. We also will show that this generalization could encompass more general situations as some of those described in LSK [17] paper. Finally we conclude in section 4 with some comments and prospects.

2   The $A + B \rightarrow 0$ Reaction.

In this section we propose to apply Thompson's approach as a means to study the two species annihilation reaction $(A + B \rightarrow 0)$, with equal initial concentrations.

For the case of two species annihilation, at first sight, we would need two differential equations to describe its chemical kinetics. However, for equal initial densities, due to the simmetry of the problem, the two equations merge into a single one. Of course, if the concentrations are equals at starting, they remain this way during the passage of the time.

The starting point of this work is the differential equation:

$$\frac{\partial \epsilon\,(r,t)}{\partial t} = D\nabla^2 \epsilon + h\langle\epsilon\rangle - K\epsilon^2, \tag{5}$$

where ϵ is the concentration of species(A or B), D is the diffusion constant, $h\langle\epsilon\rangle$ stands for an effective input rate and K is the reaction rate. The novelty presented by equation (5) as compared to the continuous approximation of the $A + A \rightarrow 0$ reaction introduced by Krug [13], is the presence of the effective input rate $h\,\langle\epsilon\rangle$. This term has been introduced in the present work as a way to account for the phenomenon of segregation, because we know that the mean value $\langle\epsilon\rangle$ decays with the time in such a way that the effective input rate $h\langle\epsilon\rangle$ also decreases in time.

As it is well known, segregation appears in these reactions due to the impossibility of self-annihilation between A (or B) species.

In order to treat the phenomena described by (5) using Thompson's approach, let us define the action:

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$$A = \int_{l^d} d^d r \left[\frac{1}{2} D \left(\nabla \epsilon \right)^2 - h \langle \epsilon \rangle \epsilon + \frac{1}{3} K \epsilon^3 + \frac{1}{2} \frac{\partial \left(\epsilon^2 \right)}{\partial t} \right]. \tag{6}$$

Equation (5) can be obtained from (6), by imposing $\delta A = 0$, for constant t.

In an analogous way to the Thompson's reasoning [15] we make the following heuristic assumptions:

a- When the integral in (6) is taken over the cube l^d in d dimensions, the absolute values of the four terms separately in (6) are all of order unity.

b- $K(l)$ is finite in the limit $l \to \infty$.

Using assumption (a),that is a scaling assumption, in the first term of (6) we have:

$$\left| \int_{l^d} d^d r \left[\frac{1}{2} D \left(\nabla \epsilon \right)^2 \right] \right| \sim l^{d-2} \langle \epsilon^2 \rangle \sim 1, \tag{7}$$

so that the mean squared value of ϵ ($\langle \epsilon^2 \rangle$) behaves as

$$\langle \epsilon^2 \rangle \sim l^{2-d}. \tag{8}$$

For the fourth term in (6),we have

$$\left| \int_{l^d} d^d r \left[\frac{1}{2} \frac{\partial \left(\epsilon^2 \right)}{\partial t} \right] \right| \sim \langle \Omega \rangle \langle \epsilon^2 \rangle l^d \sim 1 \tag{9}$$

where we have considered that

$$\epsilon \left(t \right) = \epsilon_0 \exp \left(-\Omega t \right) \tag{10}$$

Putting (8) into (9), we obtain:

$$\langle \Omega \rangle^{-1} \equiv \tau \sim l^2. \tag{11}$$

We observe that (11) points out to the signature of the brownian character of these diffusion limited reactions.

Applying hypothesis (a) to the second term of (6) leads to:

$$\left| - \int_{l^d} d^d r \left(h \langle \epsilon \rangle \epsilon \right) \right| \sim \langle h \rangle \langle \epsilon \rangle^2 l^d \sim 1 \tag{12}$$

Supposing $\langle h \rangle \sim 1$, we have for the mean value of ϵ ($\langle \epsilon \rangle$) the behavior:

$$\langle \epsilon \rangle \sim l^{-\frac{d}{2}} \tag{13}$$

Using (11) into (13), we obtain:

$$\langle \epsilon \rangle \sim \left(l^2\right)^{-\frac{d}{4}} \sim \tau^{-\frac{d}{4}} \tag{14}$$

This result (Eq. (14)) agrees with that obtained by Bramson and Lebowitz [5] which performed rigorous calculations for the $A + B \rightarrow 0$ reactions. We observe that we have treated here only the case of equal initial concentrations, namely $\langle \epsilon_A \rangle_0 = \langle \epsilon_B \rangle_0$. The case of unequal initial concentrations will be treated elsewhere.

Now let us use assumption (**a**) in the third term of (6),

$$\left| \int_{l^d} d^d r \left(\frac{1}{3} K \epsilon^3\right) \right| \sim \langle K \rangle \langle \epsilon^3 \rangle l^d \sim 1 \tag{15}$$

In order to pursue further let us make a plausible hypothesis:

$$\langle \epsilon^3 \rangle \sim \langle \epsilon^2 \rangle \langle \epsilon \rangle \tag{16}$$

This kind of decoupling could be justified taking in account that the reaction term which appears in Eq. (5) is essentially of a bilinear form (a two points correlation). Beside this we observe that this decoupling has been worked well in a previous calculation [14], where we reproduced the exact results of Peliti [12] for the $A + A \rightarrow 0$ reaction.

Using (8), (13) and (16) in (15), we obtain:

$$\langle K \rangle \sim l^{\frac{d}{2}-2} \sim \left(l^2\right)^{\frac{d}{4}-1} \tag{17}$$

By considering (11), we can write also:

$$\langle K \rangle \sim \tau^{\frac{d}{4}-1} \tag{18}$$

Equation (17) displays $d = 4$, as the upper critical dimension for the model.

We see from (17) that $\langle K \rangle$ diverges as $l \rightarrow \infty$, for $d > 4$. Then, in order to satisfy assumption (**b**) we adopt $\langle K \rangle = 1$, for $d > 4$. So the mean field description of this model is correct for $d > 4$.

Now, at the upper critical dimension $(d = 4)$, let us make some additional considerations in order to obtain the logarithmic corrections to the reactant concentration ϵ. We have for $d = 4$(see (8), (13) and (16)):

$$\langle \epsilon^3 \rangle \sim \langle \epsilon^2 \rangle \langle \epsilon \rangle \sim l^{-4}, \quad for \quad d = 4. \tag{19}$$

If we use assumption (**a**) for the third term of (6) in a somewhat modified context, and after having made inside the integral the following substitution:

$$\epsilon^3 \sim r^{-4} \tag{20}$$

we can write

$$\int_{l^d} d^d r \left(\frac{1}{3} K \epsilon^3 \right) \sim \int_1^l \left(\frac{1}{3} K r^{-4} \right) r^3 dr \sim \langle K \rangle \ln(l) \sim 1 \tag{21}$$

where l is measured in units of space lattice, being 1 the lower cutoff.

Then we have for $d = 4$,

$$\langle K \rangle \sim [\ln(l)]^{-1}. \tag{22}$$

At this point, let us consider the following differential equation:

$$\frac{1}{2} D \left(\frac{\partial \epsilon}{\partial r} \right)^2 - \frac{1}{3} \langle K \rangle \epsilon^3 = 0. \tag{23}$$

This equation can be obtained by considering the equality of the first and third terms of (6)(given by assumption a), where we suppose that we can substitute equality between integrals by equality between integrands, after replacing K by $\langle K \rangle$.

We can solve (23) at the upper critical dimension ($d = 4$), by performing the integration between 1 and l, and using (22). We get:

$$\langle \epsilon \rangle \sim \frac{\ln(l)}{l^2} \sim \frac{\ln(\tau)}{\tau}, \quad \text{for} \quad d = 4. \tag{24}$$

As we can see from (22) just at the upper critical dimension for the $A + B \to 0$ reaction $(d_c = 4)$, we have obtained a logarithmic correction to the mean field description. The same behavior was obtained before for the $A + A \to 0$ reaction at $d_c = 2$.(see [14]).

3   Unified Treatment of $A+A \to 0$ and $A+B \to 0$ reactions.

The relative success of Thompson's approach [15] in treating both $A+A \to 0$ and $A+B \to 0$ reactions encourage us to look for an extended action which could encompass the two mentioned reactions as limiting cases. So let us write the following extended action.

$$A_\sigma = \int_{l^d} d^d r \left[\frac{1}{2} D \left(\nabla \epsilon \right)^2 - h \langle \epsilon \rangle^\sigma \epsilon + \frac{1}{3} K \epsilon^3 + \frac{1}{2} \frac{\partial \left(\epsilon^2 \right)}{\partial t} \right]. \tag{25}$$

where $\sigma \geq 0$.

In an analogous ways that we have worked before, we can apply Thompson's method [15] to the action giving by (25), obtaining:

$$\langle \epsilon \rangle_\sigma \sim l^{-d/(\sigma+1)}, \tag{26}$$

and

$$\langle K \rangle_\sigma \sim \left(l^2 \right)^{\frac{d}{2\sigma+2}-1}. \tag{27}$$

Relation (27) implies that, for the model defined in (25), the upper critical dimension is given by

$$d_c \left(\sigma \right) = 2\sigma + 2. \tag{28}$$

So alternatively we can write $\langle K \rangle_\sigma$ as

$$\langle K \rangle_\sigma \sim \left(l^2 \right)^{\frac{d}{d_c}-1} \sim \tau^{\frac{d}{d_c}-1}. \tag{29}$$

We observe that if $\sigma = 0$, $d_c = 2$ and we recover the $A + A \to 0$ behavior [12,14], and putting $\sigma = 1$ we get $d_c = 4$, reproducing the results of the previous section for the $A + B \to 0$ reactions.

It is interesting to verify that the action given by (25) can reproduce the results of the LSK work [17], in the case of euclidian geometries. First we can write:

$$\langle \epsilon \rangle_\sigma \sim \tau^{-d/(2\sigma+2)} = \tau^{-d/d_c}. \tag{30}$$

Making the requirement that the exponent of right side of (30) to be equal to $-\alpha$ given by (4), and by setting $d_s = d_f = d$, we have:

$$\sigma = \frac{\gamma}{2-\gamma}. \tag{31}$$

Therefore putting $\gamma = \sigma = 0$, and $\gamma = \sigma = 1$, we get the long time behavior of the $A + A \rightarrow 0$ and $A + B \rightarrow 0$ reactions respectively. The case of $A + B \longrightarrow 0$ reactions where correlations are important (see [17]) can be described for some intermediate values of the parameters γ (or σ).

Finally is worth to point out that at the upper critical dimension of the model described by the action (25) we have again the logarithmic corrections to the mean field behavior. This result can be obtained in the same way we have worked out before in section 2. Doing this, we obtain:

$$\langle \epsilon \rangle_\sigma \sim \frac{\ln(l)}{l^2} \sim \frac{\ln(\tau)}{\tau}, \quad \text{for} \quad d_c = 2\sigma + 2. \tag{32}$$

Before concluding this section we would like to write an extendend version of the renormalized reaction rate in the same spirit of Peliti's work [12]. For long time and long wavelengths, we can write the scaling relation:

$$K_\sigma \sim \left(l^2\right)^{\frac{d}{2\sigma+2}-1} \cdot f\left(\frac{l^2}{\tau}\right). \tag{33}$$

Putting $\sigma = 0$, we recover the renormalized reaction rate of Peliti [12] (equation (10) of his paper).

4 Concluding remarks.

In this paper we have proposed a model lagrangian (action) as a means to describe a large class of diffusion limited reactions. The long time behavior of the concentration ϵ and of the reaction rate K were evaluated by using Thompson's approach [15],which can be thought as being a simple alternative way to the renormalization group method [16].

In two particular cases of this extended action, we recover the exact results of Peliti [12] for $A + A \longrightarrow 0$ and the rigorous bounds of Bramson and Lebowitz[5] for the $A + B \rightarrow 0$ reactions. Besides its simplicity, one of the advantages of the present method is that it can encompass diffusion limited reactions of different classes of universality within the same formalism. Moreover, our calculations display logarithmic behavior of the species concentrations and reactions rates at their respectives upper critical dimensions for any class of universality.

An other advantage of the present method is that it can be extended to study, for example, the scalar field theories Φ^3, Φ^4, and Φ^n for dimension d, in such a way that we can obtain a certain critical dimension d_c for a given value of n in Φ^n theory in a closed form. But now, d_c must be interpreted as a dimension where the Φ^n theory becomes renormalizable displaying logarithmic dependence of the coupling constant in the energy scale. This line of reasoning will be subject of a forthcomming paper.

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